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Item 19ABSTRACT

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Specifically, the objectives defined for this study were to:

- ( 1 ) obtain kinetic information in the low and intermediate temperature regimes (500-1000 K) over a range of pressures (up to 15 atm) for the oxidation of pure hydrocarbons in the C<sub>4</sub> to C<sub>12</sub> range;
- ( 2 ) determine the synergistic and antagonistic effects for binary and ternary mixtures of full boiling range fuel components; and
- ( 3 ) develop a method for predicting the ignition characteristics of actual fuels based on their composition.

Work focused on mechanistic studies using the static reactor, ignition studies using the atmospheric pressure flow reactor, and construction, verification, and preliminary testing of the pressurized flow reactor. The overall program has been successfully completed and has added to our understanding of fuel factors and physical effects on oxidation and ignition processes.

OXIDATION AND IGNITION CHARACTERISTICS  
OF  
HYDROCARBON FUELS

Final Report

January 1990

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## I. INTRODUCTION

### A. Motivation

Because of the diminishing availability of high-quality crude petroleum, it will become necessary in the future to turn to the use of lower grade petroleum based fuels as well as synthetic fuels derived from sources such as oil shale, coal, and tar sands. These fuels will differ from current conventional fuels in that they are likely to have higher aromatic and inorganic contents, higher end points, and lower cetane numbers. Accommodating these lower quality fuels without extensive refining and upgrading may require relaxing the current fuel specifications. Apparently, this may be the only possible way of ensuring an adequate fuel supply with reasonable economy in both refinery energy and cost (AGARD, 1982). However, attempting to use these broad specification fuels in existing combustion systems could lead to special problems in the areas of fuel stability and ignition and combustion behavior (NASA, 1979; Project Squid, 1977; AGARD, 1982; U.S. Army, 1984; Zucchetto, *et al.*, 1988; Chin and Lefebvre, 1989). Consequently, it is desirable initially to determine the usability of these fuels and then to investigate ways of making these fuels compatible with existing combustion systems or, alternatively, making combustion systems compatible with these fuels.

The Project Squid and NASA Workshops and the AGARD Advisory Report, cited above, identified several specific goals for research on general combustion processes as well as on the combustion characteristics of both conventional and broad specification fuels. One of the primary goals involved developing a fundamental understanding of the ignition process of hydrocarbon fuels with particular emphasis on the underlying chemical behavior. Research in this area is relevant to engine combustion problems that are ignition related, such as knock in spark ignition engines and misfire and cold start in diesel engines. Henein (1976) highlighted the importance of the chemistry by demonstrating that the chemical processes are rate controlling during the delay period in diesel ignition.

The compression ignition process is complex and involves preignition reactions which lead up to the point of autoignition. This is the point at which energy is liberated at a sufficient rate to sustain combustion in the absence of an external energy source, and is characterized by rapid rates of pressure and temperature rise. The tendency of a fuel to autoignite is determined by its chemical structure and the manner in which it undergoes oxidation. In order to gain insight into the autoignition characteristics of hydrocarbon fuels it is necessary to understand the kinetics of oxidation, especially that which occurs prior to autoignition. The oxidation chemistry determines the heat release rate, the reaction

intermediates, and the ultimate products of combustion. The large number of concurrent and competing chemical reactions which involve a correspondingly large number of chemical intermediate species results in a very complex mechanism for oxidation chemistry. This is the case even for small, single component fuels such as methane, and becomes exponentially more complex as the size of the fuel molecule increases. Consequently, attempting to understand the detailed chemistry of distillate fuels, which are multicomponent blends of a variety of relatively high molecular weight fuels, from direct studies of the fuels has proven to be untractable.

A somewhat more productive technique has been to develop a better understanding of the autoignition behavior of full-boiling range fuels by using a more global measure of ignition quality, rather than trying to assess the detailed chemistry of these complex fuels. This method involves the testing of the actual fuels in engines which are set up to obtain octane and cetane ratings, the most common indicators of ignition quality in use today. However, due to concerns over the applicability of these ratings with non-standard fuels, extensive testing in actual engines would likely be required. Though useful, this approach has its drawbacks in that it would require a significant amount of time, energy and equipment to perform the actual testing. Also, although these testing procedures do provide information on the ignition quality of a particular fuel, they do not provide a means to discern why a fuel behaves as it does with respect to ignition behavior.

An approach which will be successful for both the prediction of ignition quality and the assessment of ignition chemistry involves testing simple two and three component fuel blends in laboratory scale chemical reactors. With this approach, the physical factors influencing the ignition process can be controlled much more carefully than in an engine, and ignition quality can be evaluated solely in terms of the chemical effects of the fuel components on the ignition process. Single fuel components representing the different classes of hydrocarbons within a distillate fuel, such as alkanes, alkenes, and aromatics, can be blended at different ratios and tested in order to develop an understanding of how the different classes of hydrocarbons interact and which control the ignition behavior. Such studies can lead to the development of a method for predicting the ignition behavior of fuels, without extensive engine testing, based on knowledge of their composition. In view of this, a research program to study the oxidation and ignition characteristics of hydrocarbon fuels was carried out at Drexel University. This program was initiated in October 1985 with the awarding of a research grant through the Army Research Office (Grant No. DAAG 29-85-K-0253, Project No. 22437-EG) and was completed in November 1989. This final project report documents our activities on this ARO program.

## B. Objectives

The objectives defined for this study were to:

- (1) obtain kinetic information in the low and intermediate temperature ranges (500-1000 K) over a range of pressures (up to 15 atm) for the oxidation of pure hydrocarbons with carbon numbers in the C<sub>4</sub> to C<sub>12</sub> range;
- (2) determine the synergistic and antagonistic effects for binary and ternary mixtures of full boiling range fuel components; and
- (3) develop a method for predicting the ignition characteristics of actual fuels based on their composition.

## C. Methodology

The methodology of the program was to perform bench scale tests on single component pure fuels and binary and ternary mixtures of pure fuels. The fuels consisted of branched and straight chain aliphatics and aromatics, which are representative of components in distillate fuels and gasolines. The experiments were carried out over a range of reaction conditions which were representative of actual engine conditions prior to and during the ignition process. Three separate experimental test facilities were used to carry out this study: a static reactor, an atmospheric pressure flow reactor, and a pressurized flow reactor. Gas chromatographic and mass spectrometric analysis were used to determine the stable reaction intermediates and products associated with the oxidation of these fuels. Results from these studies are being used to provide kinetic information, to formulate hypotheses on ignition mechanisms, and to determine the relative effects of the various classes of components within multicomponent fuel mixtures.



## II. RESEARCH PROGRAM

As noted, this ARO sponsored program examining the oxidation and ignition characteristics of hydrocarbon fuels was initiated in October 1985 and ran through November 1989 (Grant No. DAAG 29-85-K-0253, Project No. 22437-EG). The overall objectives and methodology were just described in the previous section and, hence, are not repeated here. Following a description of the experimental facilities and procedures in Section A, an overview of the general research activities is given in Section B and a discussion of the specific research accomplishments for this program is provided in Section C. A summary of the personnel supported and their activities is presented in Section D and a list of reports, publications, and presentations currently completed or under preparation appears in Section E.

### A. Experimental Facilities and Procedures

An existing atmospheric pressure turbulent flow reactor was used in this program to establish reactivities at 1 atm. This flow system, shown in Figure 1, has been used extensively in the past for diesel odor research (e.g., Hsieh *et al.*, 1982), for carbonyl chemistry studies (Koert *et al.*, 1990) and for preignition studies (Wilk *et al.*, 1989). The flow reactor consists of a 2.3 cm diameter, 30 cm long quartz tube located inside a furnace, which allows for the study of reactions up to about 1000 K. Gas sampling was accomplished using an isokinetic sampling probe which could be positioned axially along the reaction tube. Gas samples were acquired at various points along the reaction zone, stored in a heated, multi-loop sample valve, and analyzed by gas chromatography using a Varian 3700 gas chromatograph equipped with a flame ionization detector. Good separation of reaction products for fuels such as the butanes was easily achieved with a porous-polymer packed column such as Porapak Q/R, and temperature programming. The GC was also equipped with a nickel catalyst which methanizes the carbon oxides and hydrogenates oxygenated hydrocarbons in the sample and facilitates their detection on a flame ionization detector. The type of data generated is illustrated by our work on propane and propene where the following species have been identified and their concentrations measured:  $C_3H_8$ ,  $C_3H_6$ , CO,  $CO_2$ ,  $CH_4$ ,  $CH_3OH$ , HCHO,  $CH_3CHO$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $C_3H_6O$ ,  $CH_2CHCHO$ , acetone, 1, 3-butadiene, butane, butene, and others. For our more recent work with larger hydrocarbons, capillary column separation techniques have been implemented.

To investigate the effect of pressure on reaction progress, a pressurized flow reactor of comparable size to the APFR was utilized. The pressurized turbulent flow reactor, shown in Figure 2, is designed for operation up to 1000 K and 20 atm; to date, it has been exercised to

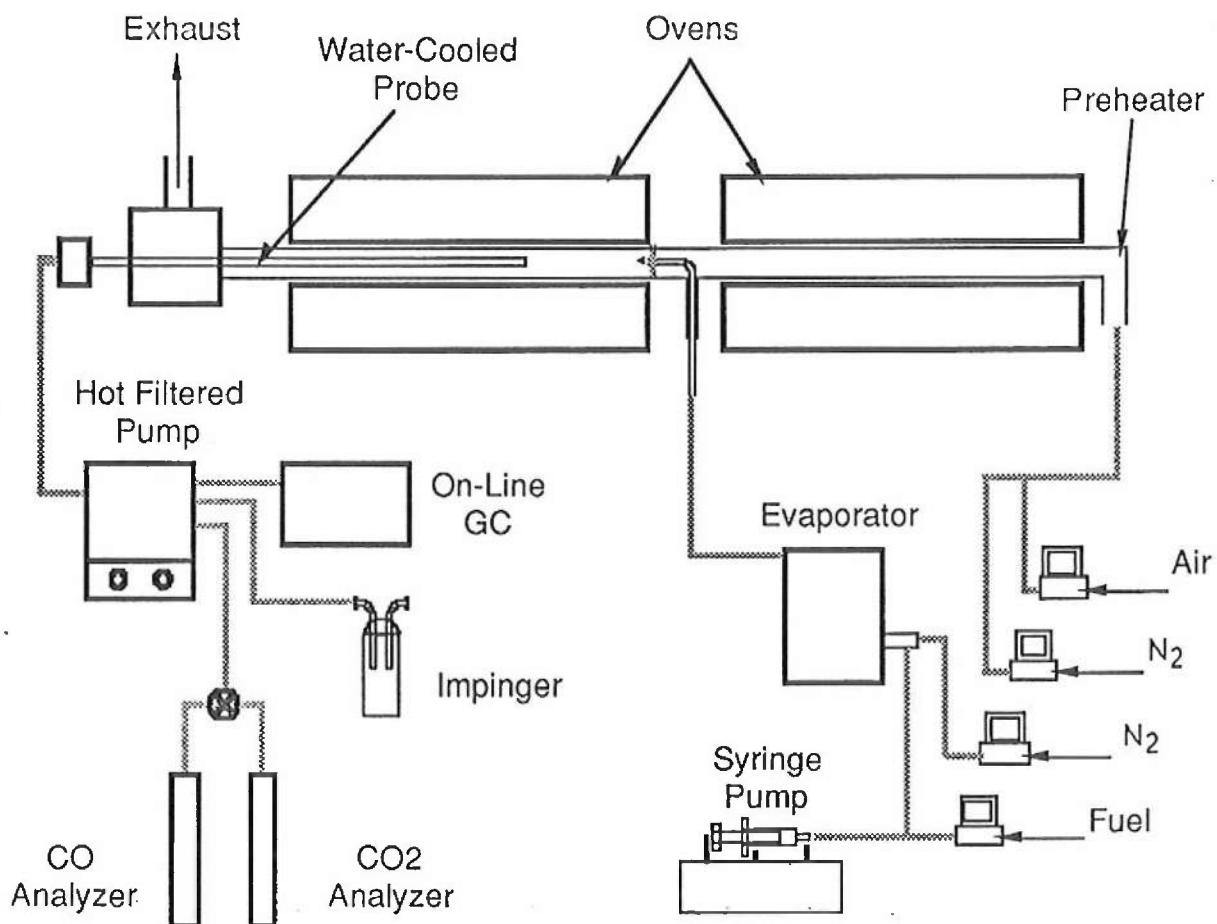


Figure 1a. Schematic of the Atmospheric Pressure Flow Reactor

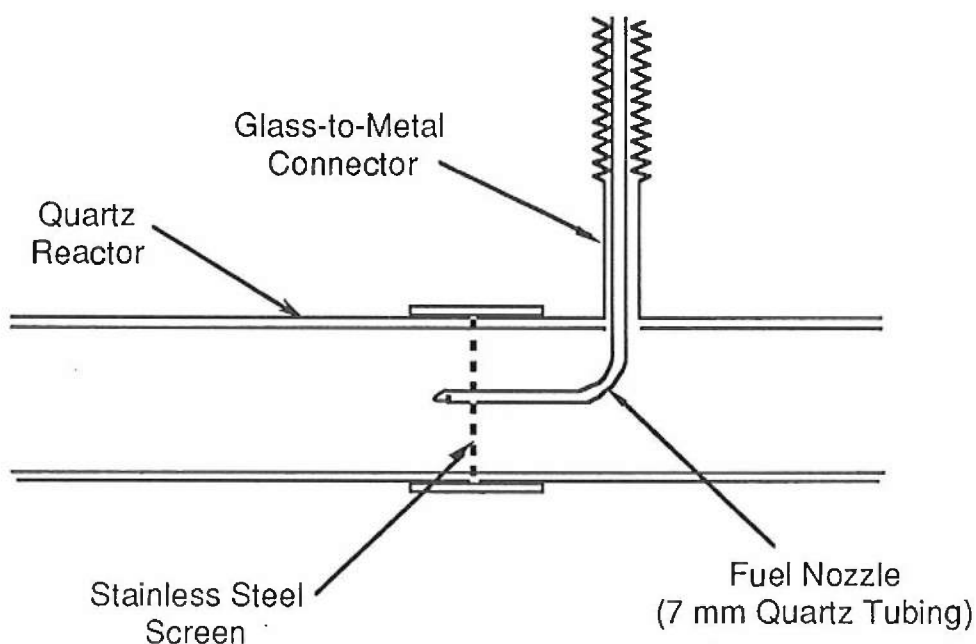


Figure 1b. Details of the Mixing Nozzle on the Atmospheric Pressure Flow Reactor

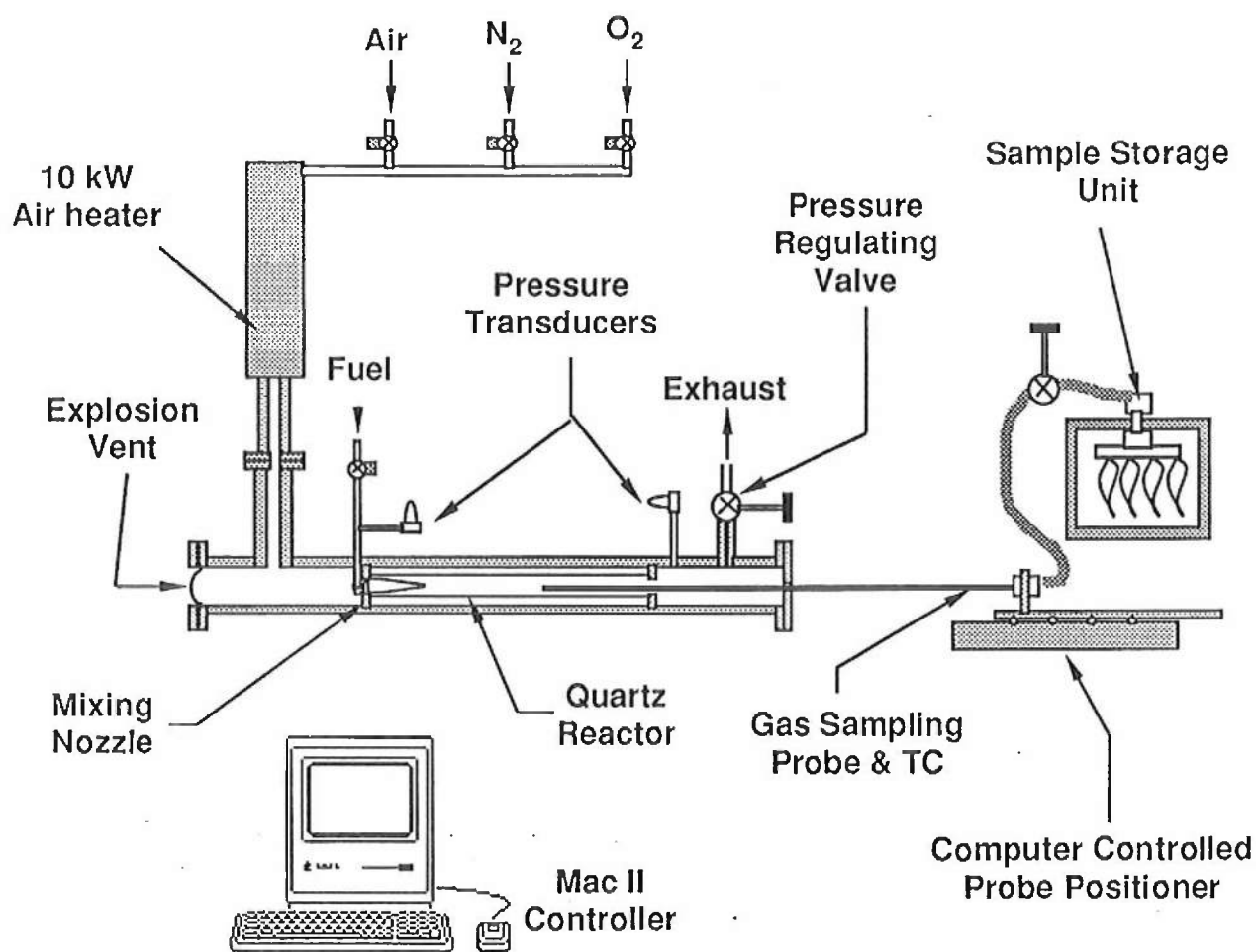


Figure 2a. Schematic of the Pressurized Flow Reactor Test Facility.

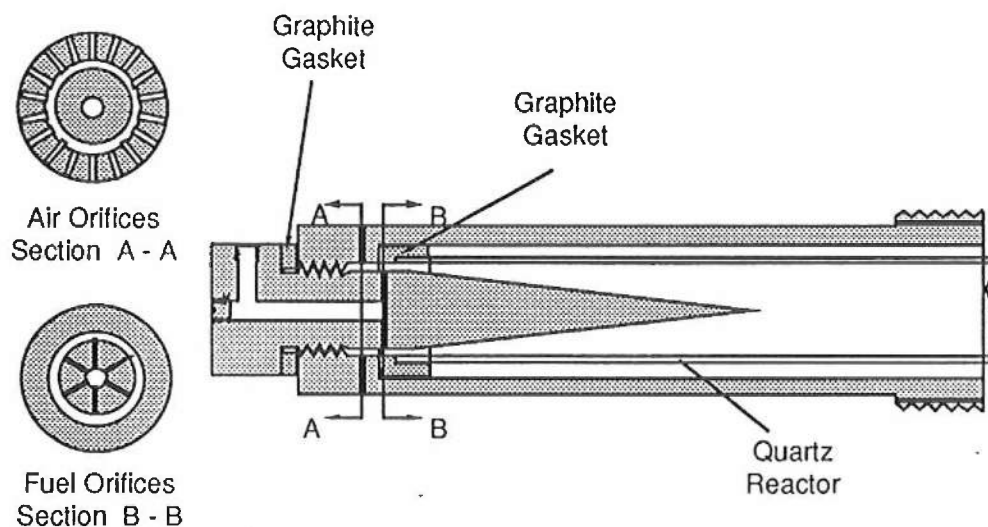


Figure 2b. Details of the Opposing Jet Annular Mixing Nozzle.

920 K and 14 atmospheres. Mass flow controllers are used to regulate and meter the flow of the oxidizer stream before it enters the 10 kW air heater. The premixed stream of air diluted with nitrogen enters the preheater at room temperature with a maximum flow rate of 700 slm at pressures up to 20 atm. The oxidizer stream leaves the preheater with a maximum temperature of 1000 K. An explosion vent is located near the inlet to the pressure vessel. A mass flow controller regulates and meters the flow of dilute gaseous fuel mixtures to the reactor, and a strain gage pressure transducer measures the pressure at the exit of the flow controller. The gaseous fuel stream is heated and mixed with the preheated oxidizer in an opposing jet annular mixing nozzle. The reactor test section is heated and lined with quartz in order to provide an adiabatic reaction zone free from wall effects. The reactor pressure is measured with a second strain gage pressure transducer at the reactor exit. Precise control of the reactor pressure is provided by means of a high pressure stainless steel metering valve. Samples of the reacting gases are withdrawn from the reactor along the centerline with a 5 ft. long, glass-lined, water-cooled gas sampling probe. A thermocouple protruding from the tip of the probe measures the temperature in the reactor 1 cm upstream of the probe tip. A water-cooled, multiple o-ring seal is used to allow the movement of the probe and prevent leaks as it passes through the wall of the pressure vessel. Control of the probe position is facilitated by the use of a stepper motor driven linear motion positioning table. Extracted gas may be directed at a variety of permanent gas analyzers for CO, CO<sub>2</sub>, and O<sub>2</sub> concentration measurements, or stored in a heated storage unit capable of holding 15 gas samples. These stored samples can then be analyzed at a later time on the gas chromatograph systems.

Proper specification of the reaction time of gas samples is necessary in order to make inferences about chemical kinetic rates and to compare measurements to modeling predictions. Thus, flow characterization in the reaction section of the APFR and the PFR has been conducted, in order to correctly convert sampling location to reaction time. Characterization of the flow field in the APFR has been made by a straight forward application of the theory of laminar flow development for internal flow in a round duct. This analysis is made possible by the design of the mixing channel in the APFR (see Figure 1b). The flow field immediately downstream of the turbulence generating stainless steel screen can be assumed to be uniform. Since the flow is laminar in the reactor, the reacting gases downstream of the screen are in the developing flow region. The operating range of the APFR is such that the exit of the reactor is approximately half of the entry length, and thus gas samples are drawn only from the core flow. In the core, the velocity is essentially uniform with no radial component, however, the fluid core undergoes a continuous acceleration in the entry region due to the encroachment of the boundary layer. A computer program has been written to calculate the velocity in the core as a function of distance from the mixing screen.

Characterization of the flow field in the PFR is more complicated due to the design of the mixing nozzle (see Figure 2b). Hotwire velocity measurements have been made in a duplicate reactor under cold flow conditions in order to obtain the radial and axial distribution of velocity and turbulence intensity. The high turbulence induced by the opposing jets in the annulus causes high turbulence intensity levels (~ 40%) which lead to the rapid attainment of a fully developed turbulent flow profile. By 2 diameters downstream from the nozzle exit plane the profile has completely flattened out, and fully developed turbulent flow is achieved by 10 diameters. With the velocity field thus characterized, residence time calculations can be performed using volumetric sampling gas sampling rates, reactant temperature and reactant pressure as input. Both a mean residence time and a residence time uncertainty result from this calculation.

An existing static reactor system also was modified and used for the examination of low pressure ignition. This system, shown in Figure 3, has been used in previous studies on ignition behavior of high molecular weight hydrocarbons such as dodecane and tetralin (Wilk *et al.*, 1985b, 1987b). It has also been used to study the detailed chemistry of lighter hydrocarbons such as propane, propene, and normal butane and isobutane (Wilk *et al.*, 1985a, 1986, 1987a; Addagarla *et al.*, 1987). The static reactor system consists of a 1.4 liter cylindrical pyrex reaction vessel located inside a temperature controlled compartment. The system is equipped with associated instrumentation for monitoring and recording the pressure and temperature as the reaction progresses. For the study of gaseous fuels, the reactants are premixed in a separate mixing vessel after which the homogeneous fuel/oxidizer mixture is admitted into the reaction vessel by way of a solenoid valve. For the study of liquid fuels, a prechamber is used to vaporize the fuel in a nitrogen bath before mixing. A Varian 3700 gas chromatograph, equipped with a flame ionization detector, and a Shimadzu 8AIT gas chromatograph, equipped with a thermal conductivity detector, are used for on-line chemical species analysis. These units are coupled directly to the static reactor system using short transfer lines and a gas sampling valve.

Species analysis from any of these facilities also is possible by GC/MS. This technique provides the ability to identify species by their mass.

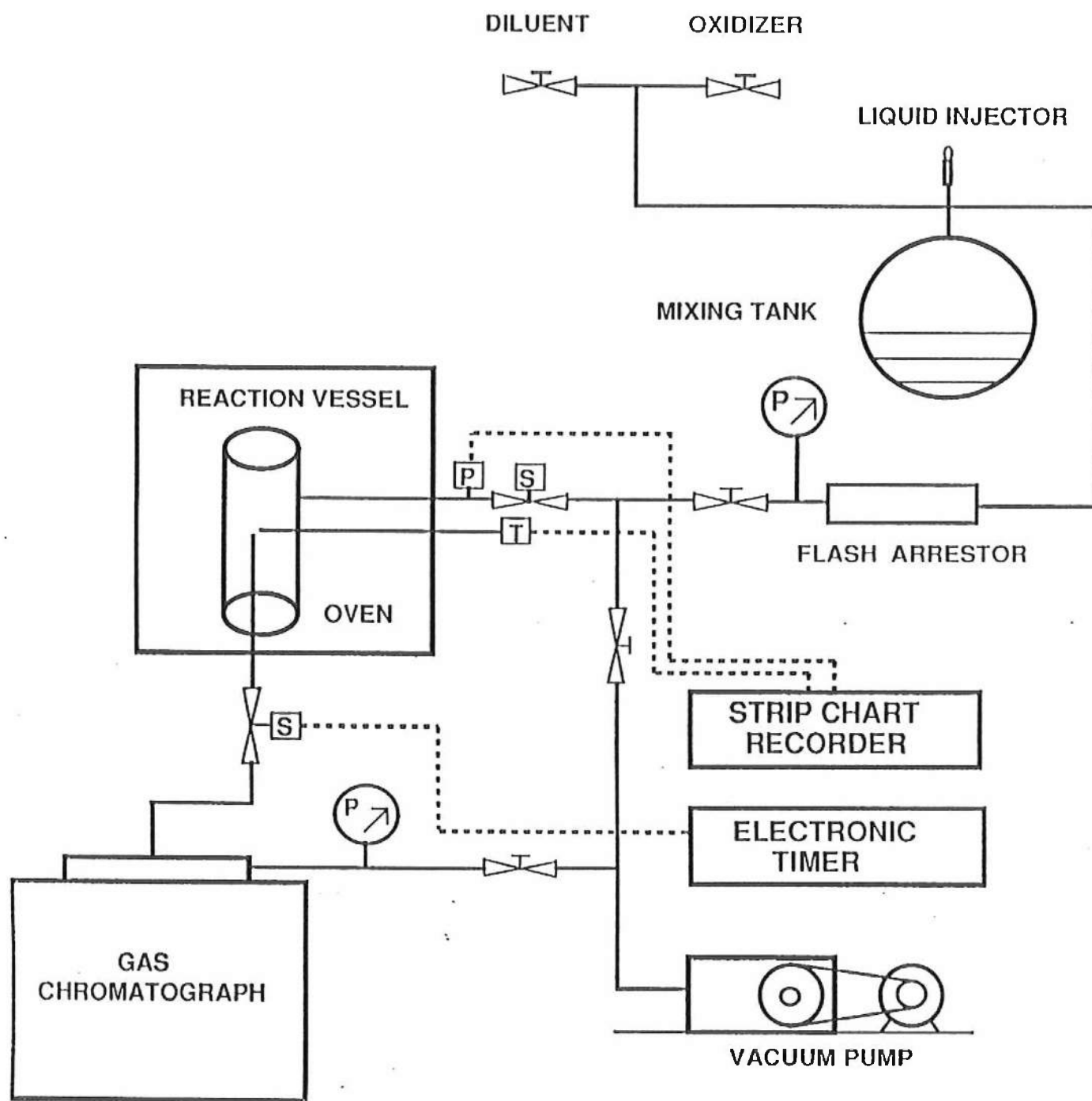


Figure 3. Schematic of the Static Reactor Experimental Facility.

## B. Program Summary

The primary efforts in this research program have been focused in three main areas: parametric studies in the static reactor (SR); parametric studies in the atmospheric pressure flow reactor (APFR); and construction, performance verification, and preliminary studies in the pressurized flow reactor facility (PFR). The parametric studies involved detailed low and intermediate temperature testing of C<sub>2</sub> and C<sub>3</sub> alkenes, C<sub>4</sub> alkanes and propene oxide in the SR, and carbonyl formation studies in the APFR. In addition, the low temperature (cool flame and two stage) ignition behavior of binary and ternary mixtures of n-octane, isooctane, dodecane, toluene, and n-pentane was examined. Studies were conducted in the pressurized facility to map the reactivity of ethane, ethene, propane, and propene as a function of pressure and temperature.

## C. Specific Research Accomplishments

A number of specific research accomplishments for the current program are identifiable. The major accomplishments are listed below along with a brief discussion of their significance.

1. The region of negative temperature coefficient was identified for n-butane oxidation over the temperature range 655-695 K. This region was determined to be one of transition from a low temperature to an intermediate temperature reaction regime based on the shift in reaction products from oxygenates to alkenes.
2. Experiments were conducted on ethene and propene in order to determine the reaction paths of alkenyl radicals (C<sub>n</sub>H<sub>2n-1</sub>). Results from the ethene studies confirmed the Baldwin-Walker theory that the reaction between vinyl and O<sub>2</sub> proceeds by a 4-center reaction leading to formaldehyde and formyl. Results from the propene studies indicate that, at these temperatures, allyl tends to react with other radicals in the system, in disproportionation reactions, and in recombination reactions with itself.
3. The low and intermediate temperature oxidation of isobutane was examined. The isobutane work complemented the work on n-butane discussed earlier. Specifically, the region of negative temperature coefficient (NTC) for isobutane was identified between 650-680 K. Chemical analysis showed there to be a distinct transition in the mechanism across this region. Comparison of these results with our previous

results for other fuels (n-butane, propene, propane) showed the mechanism transition and NTC region to be strongly dependent on the shift in equilibrium of  $\text{CH}_3 + \text{O}_2 \rightleftharpoons \text{CH}_3\text{O}_2$ . The results were also related to recent engine results on isobutane performed by Green *et al.* (1987).

4. Additional studies on isobutane oxidation were directed at determining the effects of oxygen concentration and temperature on the position of the negative temperature coefficient region and the associated mechanism shift. Studies were conducted at temperatures in the range 568-693 K for isobutane/ $\text{O}_2/\text{N}_2$  mixtures for four different oxygen concentrations. In earlier studies, analyses of product distributions indicated that the NTC region and the shift in the mechanism resulted from a shift in the position of equilibrium of the reaction of alkyl radicals with oxygen:  $\text{R} + \text{O}_2 \rightleftharpoons \text{RO}_2$ . Consequently, it appears that the temperature at which the shift occurs is dependent on three things: (1) the particular alkyl radical involved; (2) the equilibrium constant; and (3) the oxygen concentration. The third dependency was investigated in this study by varying the oxygen concentration and examining the effects on the NTC region. In general, increasing the oxygen concentration resulted in a slight shift of the NTC region to higher temperatures. These findings are relevant in the sense that practical combustion systems operate at higher pressures, and therefore, higher absolute concentrations of  $\text{O}_2$ . Thus, the effect of higher  $\text{O}_2$  concentration is to shift the point at which the mechanism switches from a low temperature regime to an intermediate temperature regime to higher temperatures.
5. Experiments were conducted to study the oxidation of propene oxide, an important intermediate in the oxidation of propene. Results showed that the mechanism of propene oxide oxidation proceeds via H atom abstraction followed by ring opening and then decomposition to products consisting of primarily formaldehyde, acrolein, and ethene.
6. During the course of this research program, we were engaged in cooperative work with Westbrook and Pitz of LLNL on the low and intermediate temperature oxidation of ethene, propene, propane, and n-butane. Results from our static reactor experiments were used to modify and extend the chemical kinetic mechanisms, originally validated at high temperatures, for use at low and intermediate temperatures where the onset of autoignition occurs. The model was successful in predicting the variation in the induction period over the region of negative



temperature coefficient and the species concentrations of intermediates and products at these temperatures from our data.

7. Experiments on pure, single-component hydrocarbons and binary and ternary hydrocarbon mixtures were performed in the static reactor. Participating in a portion of this work was Professor Hiroshi Okada from the Department of Marine Engineering, Tokyo University of Mercantile Marine, who was visiting Drexel for one month. The fuels used in these studies included n-pentane, n-octane, isooctane, toluene, and dodecane. Each fuel was oxidized alone in air to establish baseline ignition behavior. In addition, binary mixtures of n-octane/toluene, n-octane/isooctane, dodecane/toluene, and dodecane/isooctane were examined along with ternary mixtures of n-octane/isooctane/toluene. This work on liquid fuels was limited to induction period analysis obtained from the pressure and temperature-time histories of the experiments. Neither the pure isooctane/air nor the toluene/air showed any signs of reaction over the experimental conditions studied (513-613 K at  $\Phi=1.0$  and an initial pressure of 200 torr). On the other hand, the induction period data and overall activation energies obtained from the normal alkanes indicated an increasing tendency toward ignition with increasing hydrocarbon chain length. The binary blends showed that increasing amounts of the isooctane and toluene additives tended to reduce the ignition tendency by increasing the induction period, with both additives having the same inhibitory effect. The induction period data for the ternary mixtures of n-octane/isooctane/toluene showed an overall increase in induction period with an increase in total additive concentration. From the induction period data, nonlinearities in the ignition behavior due to the presence of any one component or combinations of components were not apparent and there appeared to be no synergistic effects on ignition tendency with respect to mixture composition.
8. The basic atmospheric pressure flow reactor facility was operational prior to the start of this program. However, in order to be effectively utilized for the planned ignition studies and make room for the PFR, the existing facility was relocated, refurbished, and additional instrumentation was installed to better measure and control flow rates and temperature. Also, a new sampling system was designed and constructed to permit time resolved gas sampling and detailed chemical analysis.

9. Research on the oxidation and ignition characteristics of heavier fuel components continued with the study of carbonyl formation from the oxidation of dodecane. For this work, dodecane was oxidized at temperatures from 583-888 K and at equivalence ratios ranging from 0.015 to 0.03. The carbonyl compounds were analyzed and quantified using the DNPH derivatization method and liquid chromatography, respectively. At these conditions, the only carbonyl compounds found were aldehydes. The formation of aldehydes was significant only in the 643-773 K temperature range, with the peak formation occurring at about 700 K. Concurrent CO measurements indicated a correspondence between CO formation and aldehyde formation. These results indicate a zone where the reaction rate slows significantly starting at 700 K, corresponding to the NTC region. The use of a CO concentration measurement to indicate significant reactivity in this temperature range and to locate the NTC region was demonstrated. The formation of aldehydes below 700 K and the observed inhibition of the reaction above 700 K was explained chemically by an alkylperoxy radical dominated mechanism, which included the alkylperoxy radical isomerization and decomposition (APRID) scheme.
10. The APFR work resumed with studies examining the effects of fuel structure and blending on autoignition. The APFR was used to oxidize several fuels and binary fuel blends consisting of straight chain and branched alkanes, alkenes and aromatics. The effects on autoignition tendency were investigated at temperatures in the range 570-920 K which encompassed the low and intermediate temperature reaction regimes. CO concentration was measured at the exit of the reactor as the temperature was varied. The degree of CO production was used as a measure of reactivity or autoignition tendency. A maximum in the CO concentration was observed for nearly all fuels and occurred at approximately 675 K. The decrease in the CO production above 675 K indicated a decrease in the overall oxidation rate which was attributed to the negative temperature coefficient behavior. n-Heptane was used as a baseline fuel and blended in binary mixtures with aromatics, alkenes, isooctane, and MTBE. The aromatic components, isooctane, and MTBE all inhibited the oxidation of n-heptane. The alkenes inhibited the low temperature oxidation but promoted the intermediate temperature reaction. For the n-alkanes, a good correlation was obtained between the maximum low temperature CO production and cetane number.
11. The construction of the PFR test facility has been completed and tests have been conducted to verify system operation.

12. Hot wire anemometer measurements in a PFR mock-up have been conducted to characterize the flow field within the PFR. The results of this study will be used to calculate simple residence time as a function of sampling location. Turbulence intensity measurements resulting from this study have permitted more accurate assessment of mixing time in the PFR mixing nozzle.
13. Follow-up experiments are underway on the blending effect of higher hydrocarbons on autoignition studies. The fuels being studied include typical diesel fuel components and the primary reference fuels, n-heptane and Isooctane. Previous correlations between the maximum CO concentration and octane number have been improved.
14. Modifications to the static reactor facility have been made to improve capabilities for studies of liquid fuels. To investigate chemical reaction pathways of the preignition oxidation of these fuels, there is a need to prevaporize and mix them with the oxidizer/diluent before introduction into the reactor vessel. A stainless steel 40 liter gas tank is being used as a mixing chamber for fuel-oxygen-nitrogen mixtures. The chamber is initially evacuated, and the fuel is injected and flash evaporated. Oxidizer and diluent are then introduced to complete the mixture. The bottom of the tank is slightly heated to promote mixing, and the stainless steel supply line to the reactor vessel is also heated to prevent condensation. Studies to examine the detailed low and intermediate reaction chemistry of pentane have been initiated.
15. Studies mapping the effect of pressure on reactivity of propane, propene, ethane, and ethene have begun. In these studies the PFR is being operated similarly to the APFR in studies (9 & 10) above, measuring CO production with respect to varying pressure and temperature. This work will be followed by experiments measuring the full product distribution from the pressurized preignition oxidation of propane and propene.

#### D. Research Personnel and Activities

This research project was coordinated under the supervision of Dr. Nicholas P. Cernansky (Hess Chair Professor of Combustion) as Principal Investigator. He had overall responsibility for conducting, directing, and reporting the various phases of the research program. However, the primary responsibility for carrying out and implementing the details of the experimental and analytical aspects of the program fell on the other technical personnel supported by the project. Dr. Richard D. Wilk (Ph.D.-1986; Research Scientist) earned his degree with support from this program and continued his involvement as a Post Doctoral Fellow with special responsibility for the atmospheric pressure flow reactor. Ms. Patricia A. Partridge (M.S.-1986; Ph.D. candidate [expected June 1990]) was primarily responsible for static reactor operation, gas chromatographic method development, sample collection and analysis, and data interpretation. Mr. David N. Koert (Ph.D. candidate [expected March 1990]) designed and oversaw the construction of and experimentation with the pressurized flow reactor. He also was responsible for development of liquid chromatographic techniques. Mr. Robert J. Tidona (Research Engineer) was involved in facilities maintenance and upgrading. Over the course of the research program, Dr. David L. Miller (Assistant Professor) became involved, without ARO support, in the activities of the group. This participation has resulted in his becoming a Co-Principal Investigator in subsequent programs. In addition, several undergraduate students have participated in the research program through Independent Study and Research activities or as Laboratory Aides.

## E. Reports, Publications, and Presentations

Work accomplished as part of this research program has contributed to and resulted in the following publications, reports and presentations:

1. Wilk, R.D., Cernansky, N.P., and Cohen, R.S., "Transition in the Oxidation Chemistry of n-Butane From Low to Intermediate Temperatures", Paper No. WSSCI 85-31 presented at the Fall Meeting of the Western States Section/The Combustion Institute, Davis, CA, October 1985.
2. Wilk, R.D., Miller, D.L., and Cernansky, N.P., "Intermediate Temperature Oxidation of Alkenes: Reactions of Alkenyl Radicals", Paper No. WSSCI 86-6 presented at the Joint Spring Meeting of the Canadian and Western States Sections/The Combustion Institute, Banff, Alberta, Canada, 28-30 April 1986.
3. Wilk, R.D., "Preignition Oxidation Characteristics of Hydrocarbon Fuels", Ph.D. Thesis, Drexel University, June 1986.
4. Wilk, R.D., Miller, D.L. and Cernansky, N.P., "An Experimental Study of Isobutane Oxidation at Transition Temperatures", Paper No. WSSCI 86-32 presented at the Fall Meeting of the Western States Section/The Combustion Institute, Tucson, AZ, 27-28 October 1986.
5. Wilk, R.D., Miller, D.L., and Cernansky, N.P., "An Experimental Study of the Oxidation of Propene Oxide", Paper No. ESSCI 86-61 presented at the Fall Meeting of the Eastern States Section/The Combustion Institute, San Juan, Puerto Rico, 15-17 December 1986.
6. Wilk, R.D., Cernansky, N.P., and Cohen, R.S., "An Experimental Study of Propene Oxidation at Low and Intermediate Temperatures", Combustion Science and Technology **52**, 1&2, 39-58, 1987.
7. Koert, D.N., Wilk, R.D., Partridge, P.A., and Cernansky, N.P., "Carbonyl Formation From a Model Diesel Fuel", Paper No. APCA 87-1.2 presented at the 80th Annual Meeting of the Air Pollution Control Association, New York, NY, 22-26 June 1987.
8. Addagarla, S., Wilk, R.D., Miller, D.L., and Cernansky, N.P., "Temperature and Stoichiometry Effects on Isobutane Oxidation", Paper No. WSS/JAP CI 87-23 presented at the Joint Meeting of the Japanese and Western States Sections/The Combustion Institute, Honolulu, HI, 22-25 November 1987.
9. Wilk, R.D., Cernansky, N.P., and Okada, H., "Preignition Characteristics of Higher Hydrocarbon Fuels", Paper No. WSS/JAP CI 87-24 presented at the Joint Meeting of the Japanese and Western States Sections/The Combustion Institute, Honolulu, HI, 22-25 November 1987.
10. Pitz, W.J., Wilk, R.D., Cernansky, N.P., and Westbrook, C.K., "The Oxidation of n-Butane at Low and Intermediate Temperatures: An Experimental and Modeling Study", Paper No. WSSCI 88-51 presented at the Spring Meeting of the Western States Section/The Combustion Institute, Salt Lake City, UT, 21-22 March 1988.

11. Wilk, R.D., Koert, D.N., and Cernansky, N.P., "Fuel Structure and Blending Effects on Autoignition," Paper No. WSSCI 88-52 presented at the Spring Meeting of the Western States Section/The Combustion Institute, Salt Lake City, UT, 21-22 March 1988.
12. Wilk, R.D., Pitz, W.J., Westbrook, C.K., and Cernansky, N.P., "Chemical Kinetic Modeling of Ethene Oxidation at Low and Intermediate Temperatures", Paper No. WSSCI 89-31 presented at the Spring Meeting of the Western States Section/The Combustion Institute, Pullman, WA, 20-21 March 1989; also, submitted to the Twenty-Third Symposium (International) on Combustion, Orleans, France, 22-27 July 1990.
13. Wilk, R.D., Cernansky, N.P., Pitz, W.J., and Westbrook, C.K., "Propene Oxidation at Low and Intermediate Temperatures: A Detailed Chemical Kinetic Study", Combustion and Flame **77**, 2, 145-170, 1989.
14. Wilk, R.D., Koert, D.N., and Cernansky, N.P., "Low Temperature CO Formation as a Means of Assessing the Autoignition Tendency of Hydrocarbons and Hydrocarbon Blends", Energy and Fuels **3**, 3, 292-298, 1989.
15. Wilk, R.D., and Cernansky, N.P., "The Role of Olefins in the Autoignition Chemistry of Paraffin Hydrocarbons", Paper No. ESSCI 89-14 presented at the Fall Meeting of the Eastern States Section/The Combustion Institute, Albany, New York, 30 October - 1 November 1989.
16. Koert, D.N., and Cernansky, N.P., "A Pressurized Flow Reactor for Studies of Homogeneous Gas-Phase Hydrocarbon Oxidation Through the NTC Region", Paper No. ESSCI 89-17 presented at the Fall Meeting of the Eastern States Section/The Combustion Institute, Albany, New York, 30 October - 1 November 1989.
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20. Koert, D.N., Wilk, R.D., and Cernansky, N.P., "Aldehyde Formation at Conditions Typical of Vehicle Exhaust Systems", Environmental Science and Technology, 1990 (submitted).
21. Koert, D.N., "Effects of Pressure on Hydrocarbon Oxidation Chemistry", Ph.D. Thesis, Drexel University, Philadelphia, PA, 1990.
22. Partridge, P.A., "Preignition of Pentane in Low and Intermediate Temperature Regimes", Ph.D. Thesis, Drexel University, Philadelphia, PA, 1990.

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